PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 2, 02NFC23(3pp) (2012)

Microwave Absorbing by Conducting Hybrid Nanocomposites Based on Magnetite Nanoparticles

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(Received 20 June 2012; published online 24 August 2012)

Microwave absorbing properties of hybrid nanocomposites of Fe_3O_4 nanoparticles with carbon nanotubes and polyaniline (PANI) doped with dodecylbenzenesulfonic acid have been studied. It has been found that the the addition of nanostructured components increases the absorbtion of the nanocomposites. Moreover, CNTs affect the absorbtion in high frequency range, and Fe_3O_4 nanoparticles – in low frequency range. Introduction of conductive PANI into the matrix enhances the influence of nanomaterials on the absorbance of the films.

Keywords: Nanocomposite, Magnetic nanoparticles, Absorbtion.

PACS numbers: 68.65. – k, 73.22. – f

1. INTRODUCTION

Currently a considerable interest to hybrid composite materials (HCM) based on ferromagnetic nanoparticles, carbon nanotubes (CNT) and intrinsically conducting polymers (ICP) e.g. polypyrrole or polyaniline (PANI) has been observed [1-3]. Naturally, this attention to HCM stems from expectations of researchers and manufacturers that a synergetic combination of electrical and magnetic properties of these components in their composites can be both observed and implemented in their applications for such important fields as photonics, sensing, medical and biological treatment, therapy, electromagnetic interference (EMI) shielding etc. Preparation of these materials is based mainly on two approaches – synthesis of the ferromagnetic and/or ICP component in a presence of CNT [4] or their simple mixing [5]. The synthetic approach to create HCM is obviously better as it allows formation of an intimate contact between all participants of the system during the synthesis [6]. However, to apply this approach to synthesize e.g. nanocomposites of CNT with magnetic iron oxide nanoparticles a functionalization of the CNT surface is needed in some cases [1,2]. But in turn, the oxidative modification of CNT can lead to change their mechanical strength and conductivity that should be taken into account when application of the modified CNT in the composites. To avoid the mechanical problem, here we used the both approaches through preparation of flexible robust HCM films, which united nanocomposite of CNT with Fe_3O_4 and composite of common polymer polyvinylidene fluoride (PVDF) (being a binder matrix) with PANI in conducting nanocomposite materials.

2. MATERIALS AND METHODS

The Fe_3O_4-CNT nanocomposite was prepared through growth of Fe_3O_4 nanoparticles in a presence of CNT in the joint alkaline solution of Fe^{2+} and Fe^{3+} salts similar to [4]. In most cases CNT were treated with concentrated nitric acid to create at their surface an enough quantity of centers of precipitation of Fe_3O_4 nanocrystals [2]. Application of this technique allowed quite homogeneous distribution of the nanocrystals in the nanocomposite (Fig. 1).

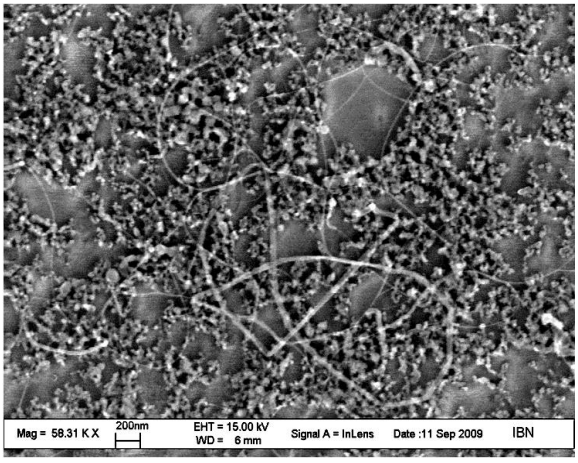

Fig. 1 – Scanning electron microscopy (SEM) image of the synthesized Fe_3O_4-CNT nanocomposite

PANI-PVDF core-shell composites were prepared by the typical chemical oxidative polymerization of aniline in presence of PVDF submicron particles in accord with the method described elsewhere [7]. As matri[polymer we used PVDF latex Kynar (Arkema) with 200 nm particles. Dodecylbenzenesulfonic acid (Acros Organics) was used as acid-dopant. Commercial multiwalled CNT and reagents to synthesize Fe_3O_4 nanoparticles were used as received.

The flexible film samples of 9mm diameter and were made by compression molding at 200 °C under the load of 10 tons. There were prepared samples series C of mixtures of the parent PVDF with different contents of the Fe_3O_4-CNT nanocomposite (set I) and samples series S of the PANI-PVDF core-shell composites with different contents of the Fe_3O_4-CNT nanocomposite (set II).

Absorption of electromagnetic energy of these mate-

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rials was measured in the frequency range 0.2 – 20.0 GHz) with the help of Agilent N5230A instrument equipped with Agilent 85070E probe.

3. RESULTS

Typical absorption spectra of the sets I and II are shown in Fig. 2.

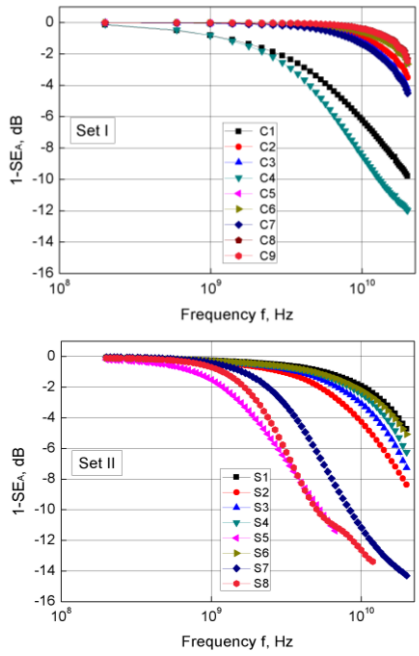

Fig. 2 – Shielding effectiveness of the set I (top) and set II (bottom), normalized for thickness d = 1 mm

As one can see from these spectra and results of their treatments (Table 1 and Table 2), the best microwave absorbing is displayed by the nanocomposite films filled with maximum content of CNT (samples C1, C4, S5, S7, S8). The sample only with CNT (S8) has the strong absorption ability, but addition of magnetic nanoparticles causes widening the absorption spectrum to lower frequencies (S5).

It is shown that addition of PANI component to the nanocomposite (transition from the set I to the set II) significantly affects the microwave absorbing of the film materials.

4. CONCLUSION

The influence of the ferromagnetic component on the absorbance of the composites is extended not only to the low-frequency part of the investigated range, but also to the high-frequency range. Introduction of the conducting components into the matrix also facilitates separation of ferromagnetic nanoparticles and the lowering of the magnetic interaction between them [3].

On the whole, the developed three and four component film nanocomposites based on magnetic Fe_3O_4 nanoparticles demonstrate good microwave absorbing in gigahertz frequency range. We believe that the achieved parameters are the result of synergetic combination of properties of the all components. This suggests that thorough selection of the nanocomposites composition and their technology of preparation can help to enhance the protection properties of these materials.

Table 1. Nanocomposite film characteristics of the set I

Sample name	CNT: Fe_3O_4	d, μm	Absorbtion coefficien α, m-1				Film tansparency, dB				Transparency for d = 1 mm, dB			
Frequency, GHz			0.2	1	10	20	0.2	1	10	20	0.2	1	10	20
C1	1:1	200	34.3	188	1438	2254	-0.03	-0.16	-1.25	-1.96	-0.15	-0.82	-6.25	-9.79
C2	1:20	240	2.53	9.02	225	806	-0.003	-0.009	-0.23	-0.84	-0.01	-0.04	-0.98	-3.5
C3	1:15	236	3.23	11.7	299	976	-0.003	-0.012	-0.31	-1.0	-0.01	-0.05	-1.3	-4.24
C4	1:2	191	23.5	188	1964	2758	-0.02	-0.16	-1.63	-2.29	-0.10	-0.82	-8.53	-12.0
C5	1:5	191	3.08	8.53	140	600	-0.003	-0.009	-0.14	-0.61	-0.01	-0.04	-0.61	-2.61
C6	1:20	181	2.57	6.65	138	611	-0.002	-0.005	-0.11	-0.48	-0.01	-0.03	-0.60	-2.65
C7	1:10	200	3.79	13.9	322	1036	-0.003	-0.012	-0.28	-0.9	-0.02	-0.06	-1.4	-4.5
C8	no	183	2.39	4.23	93.1	538	-0.002	-0..003	-0.07	-0.43	-0.01	-0.02	-0.4	-2.34
C9	no	162	2.36	4.35	95.5	564	-0.002	-0.003	-0.07	-0.4	-0.01	-0.02	-0.4	-2.45

Table 2 – Nanocomposite film characteristics of the set II

Sample name	CNT: Fe_3O_4	d, μm	Absorbtion coefficient α, m-1				Film tansparency, dB				Transparency for d = 1 mm, dB			
Frequency, GHz			0.2	1	10	20	0.2	1	10	20	0.2	1	10	20
S1	1:20	160	19.3	59.0	443	1089	-0.01	-0.04	-0.31	-0.76	-0.08	-0.26	-1.93	-4.73
S2	1:5	185	16.1	82.3	983	1925	-0.01	-0.07	-0.79	-1.55	-0.07	-0.36	-4.27	-8.36
S3	1:10	80	27.6	80.8	709	1671	-0.006	-0.03	-0.25	-0.58	-0.12	-0.35	-3.08	-7.26
S4	1:15	60	23.6	65.4	561	1441	-0.006	-0.02	-0.15	-0.38	-0.10	-0.28	-2.44	-6.26
S5	1:1	190	47.7	351	-	-	-0.04	-0.29	-	-	-0.21	-1.52	-	-
S6	1:20	150	20.7	64.9	506	1168	-0.01	-0.04	-0.33	-0.76	-0.09	-0.28	-2.20	-5.07
S7	1:2	160	10.2	96.7	2575	3293	-0.007	-0.06	-1.68	-2.15	-0.44	-0.42	-11.2	-14.3
S8	no Fe_3O_4	220	21.3	162	2910	-	-0.02	-0.15	-2.78	-	-0.09	-0.70	-12.6	-

AKNOWLEDGEMENTS

Authors are grateful to the State scientific and technical program "Nanotechnologies and Nanomaterials" for a financial support of this study.

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